Murphree tray efficiency is determined for such a binary pair. One then has the option of either using the efficiency so calculated for all of the remaining components or repeating the procedure for all possible binary pairs. Such detailed estimates of component efficiencies are then used as inputs to advanced process simulators such as ASPEN.

Issues Relating to Scale-up of Efficiency Data

Since the point efficiency data and correlations (like eqn [10] are (or should be) based on local conditions, they should, in principle, remain valid on all scales. They are then integrated with flow conditions to predict the overall tray efficiency. Correlations such as eqn [11], which provide this function of integrating the point efficiency to provide tray efficiency, do not remain valid at all scales. It has been well documented that the liquid flow patterns change quite dramatically depending on the diameter of the column and the location of the weirs near the downcomer. In future one can expect *computational fluid dynamics* to provide detailed flow information using models that remain scale invariant over a wide range of diameters.

Concluding Remarks

A series of correlations taken from the literature are presented. They permit the evaluation of the performance of a sieve tray, once a set of design parameters has been chosen as outlined in Part I. At the design stage of a new sieve tray column, one can embed this design and performance analysis steps into an optimization procedure, in such a way that the design parameters may be altered until a specified objective function is satisfied. The objective function could be a cost function that includes the capital cost of the equipment (which determines the column diameter, tray spacing, etc.) and operating costs (which determine the reflux and reboil rates and the number of ideal stages).

See also: **II/Distillation:** Historical Development; Instrumentation and Control Systems; Theory of Distillation; Tray Columns: Design; Packed Columns: Design and Performance; Vapour-Liquid Equilibrium: Correlation and Prediction; Vapour-Liquid Equilibrium: Theory.

Further Reading

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Vapour–Liquid Equilibrium: Correlation and Prediction

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Introduction

Distillation is a process used to separate liquid mixtures into two or more streams, each of which has a composition that is different from that of the original mixture. The process involves both the vaporization of the original liquid in order to generate the vapours and the subsequent condensation of the vapours to form the desired liquid products. It is evident that vapour–liquid equilibria (VLE) are essential to this separation process. Typical temperature–composition (T–x–y) diagrams, pressure–composition (P–x–y) diagrams, and vapour–liquid composition (x–y) diagrams for completely miscible binary systems are depicted in **Figure 1**.

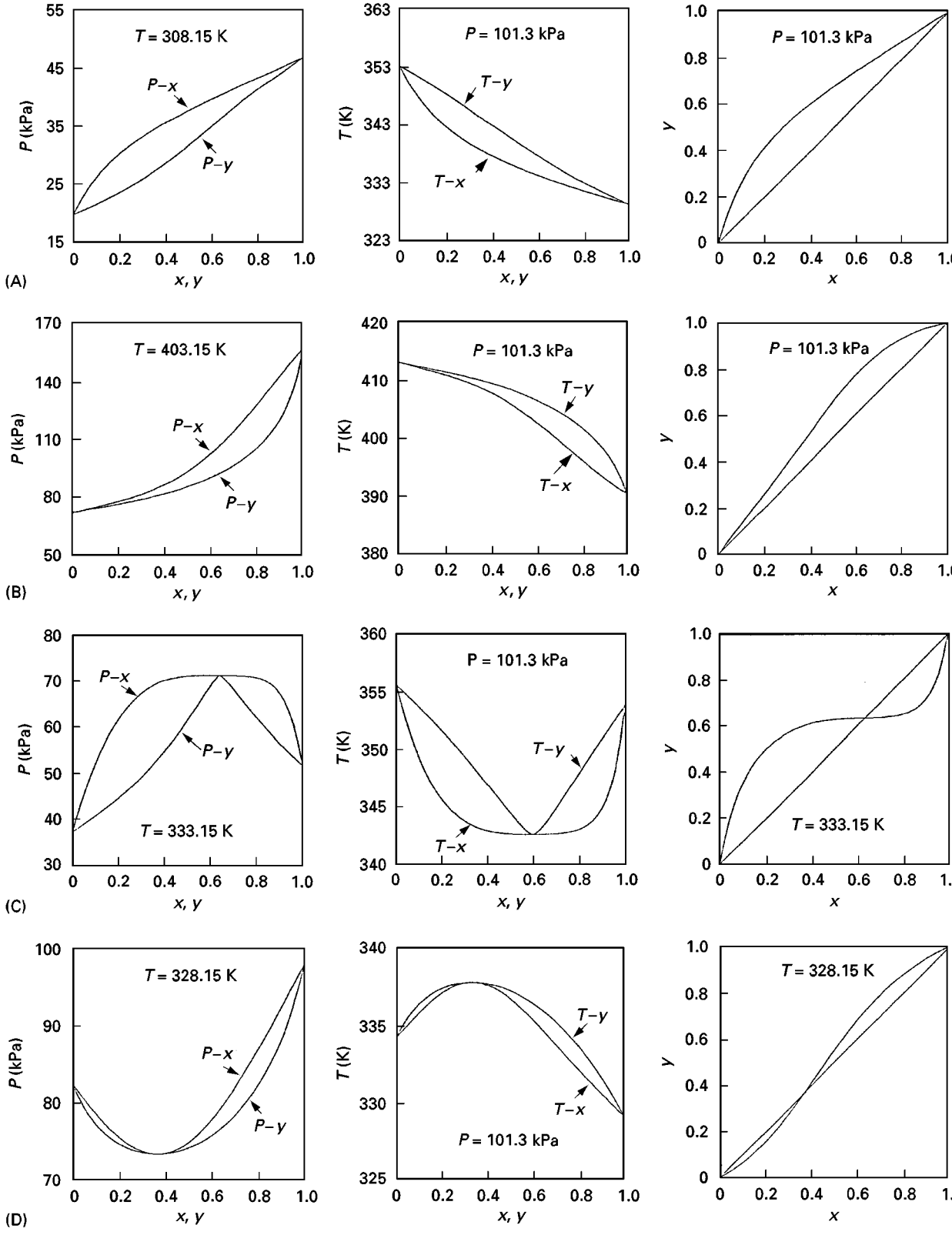

Figure 1 Four types of binary *P–x–y*, *T–x–y* and *x–y* equilibrium phase diagrams. Correlation curves are for: (A) System acetone + benzene. (B) System 1-butanol + acrylic acid. (C) System cyclohexane + 2-propanol. (D) System acetone + chloroform.

Consider an N-component closed system in which a liquid mixture at temperature T and pressure P is in equilibrium with a vapour mixture at the same temperature and pressure. The condition of thermodynamic equilibrium is that the chemical potentials of the components in both phases must satisfy the equality relation:

$$\mu_{iV} = \mu_{iL} \qquad (i = 1, 2, \ldots, N) \qquad \text{(constant } T\text{)} \quad [1]$$

The introduction of the quantity called fugacity by G.N. Lewis has facilitated the application of this condition. The fugacity of a system, f, at constant temperature is defined in the following two equations:

$$\mathrm{d}G = RT\,\mathrm{d}\ln f \quad [2]$$

and:

$$\lim(f/P) = 1 \qquad \text{as } P \text{ approaches zero} \quad [3]$$

where, in eqn [2], G is the molar Gibbs energy.

The fugacity of a component i in a solution is related to the chemical potential of the same component by the equation:

$$\mathrm{d}\mu_i = RT\,\mathrm{d}\ln \hat{f}_i \quad [4]$$

A practical expression for vapour–liquid equilibrium consideration thus takes the form:

$$\hat{f}_{iV} = \hat{f}_{iL} \quad [5]$$

where the subscripts V and L indicate fugacity in the vapour phase and liquid phase, respectively. Correlation and prediction of vapour–liquid equilibria must satisfy the equal fugacity condition. The main concern is to relate these fugacities to T, P, and the compositions of the liquid and vapour phases.

Design of distillation operations requires reliable experimental vapour–liquid equilibrium values for conditions corresponding to the desired operation. Available data may frequently be either fragmentary or for conditions different from the desired operating conditions. On many occasions, the needed experimental values are not available at all. In order to make suitable interpolation and extrapolation of the available data, and to make acceptable estimates of unavailable data, it is necessary to take advantage of the limited data available and apply prediction methods developed on the basis of reasonable assumptions. In this article, discussion is limited to correlation and prediction of the vapour–liquid equilibrium values for organic and nonelectrolyte mixtures at conditions such that Raoult's law cannot be used to represent the behaviour of all components over the complete concentration range. The emphasis is placed on the equilibrium T–P–x–y.

Correlation of Vapour–Liquid Equilibria (VLE)

The quality of the available experimental data is the first concern of any VLE correlation. It is known that a considerable proportion of experimental values are not of good quality owing to the impurity of the chemicals and poor equilibrium stills used, equipment set-ups, and operator errors. In many instances there are quantitative discrepancies among the experimental results for the same system investigated under the same thermodynamic conditions by different authors. Therefore, it is desirable to determine whether the available experimental values are thermodynamically consistent prior to correlation. Consistency tests can be applied whenever the measured properties are more than those that are needed, on the basis of the phase rule, to define the intensive properties of the system under consideration. Although the thermodynamic consistency of experimental data does not guarantee their correctness, inconsistent data are definitely not acceptable.

There are two frequently used methods in correlating vapour–liquid equilibria. One is through the gamma–phi approach, and the other is by means of an equation of state. A comparison of the two methods is presented in **Table 1**.

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Thermodynamic Consistency Test of Data

The Gibbs–Duhem equation is a differential equation that represents the interrelationship among the changes of T, P and composition (in terms of chemical potentials) of an equilibrium system. The equation has the form:

$$-ns\,\mathrm{d}T + nv\,\mathrm{d}P - \sum n_i\,\mathrm{d}\mu_i = 0 \quad [6]$$

When the Gibbs–Duhem equation is applied to the experimental results for systems under isothermal conditions and at low to moderate pressures, eqn [6] is reduced to $\sum n_i\,\mathrm{d}\mu_i = 0$. In terms of liquid activity coefficient, which is defined by:

$$\gamma_i = \hat{f}_{iL}/x_i f_i^{\mathrm{sat}} \quad [7]$$

the simplest expression for testing thermodynamic consistency has the form:

$$\sum x_i\,\mathrm{d}\ln\gamma_i = 0 \quad [8]$$

Table 1 Comparison of vapour–liquid equilibrium calculation methods

Method	*Gamma–phi approach*	*Equation-of-state approach*
Advantage	Applicable to a wide variety of mixtures, including polar systems, electrolytes, and polymers.	Applicable to a given system over wide ranges of temperature and pressure, including the supercritical region
	Simple solution models suffice for the correlation of vapour–liquid equilibrium data.	Thermodynamic properties, such as the enthalpy and entropy, can be consistently calculated from the same equation of state.
Disadvantage	Difficult to apply to systems involving supercritical components.	A single equation cannot represent the properties of all components precisely at the same time.
	Additional correlations must be used to represent the volumetric behaviour and thermal properties.	Conventional mixing and combining rules are not applicable to systems containing polar components, polymer molecules, or electrolytes.

In eqn [7], the standard-state fugacity, f_i^{sat}, is the fugacity of component i at the system temperature. The standard state is usually taken to be the pure liquid at the T and P of the system. As data for binary systems are the basis for further correlation, it is desirable to have their consistency tested first. The simplest method is the 'visual test', which is independent of the models of equations used for expressing the excess Gibbs energy. A brief description of the visual test method is presented in **Table 2** with examples depicted in **Figure 2**. More precise testing methods, such as the point-by-point test and the area test, which take into consideration the effect of temperature change on the data for systems at isobaric conditions or the effect of pressure change on the data for systems at isothermal conditions, are available. However, excess enthalpies or volume changes owing to the mixing of components may be required. Whenever the liquid activity coefficients obtained from experimental data can be represented by an integrated Gibbs–Duhem equation (an appropriate modelling equation for γ), the data are considered thermodynamically consistent. For high pressure VLE, testing methods such as those developed by Won and Prausnitz in 1973 and Christiansen and Fredenslund in 1975 may be applied.

Gamma–Phi approach

In the gamma–phi approach, the dimensionless fugacity coefficients ϕ and the activity coefficients γ are used to describe the vapour phase and the liquid phase:

$$\hat{f}_{iV} = \hat{\phi}_i y_i P \qquad [9]$$

$$\hat{f}_{iL} = \gamma_i x_i f_i^{\text{sat}} \qquad [10]$$

The fugacity coefficients can be calculated from the vapour phase PTv composition data by means of an equation of state, such as the virial equation. When the system pressure is low, either of the volume-explicit virial equation and the pressure-explicit virial equation may be truncated after the second term and used for the calculation. The resulting expressions are respectively:

$$\ln \hat{\phi}_i = (P/RT)\left(2\sum y_i B_{ij} - B\right) \qquad [11]$$

and:

$$\ln \hat{\phi}_i = (2/v)\sum y_i B_{ij} - \ln Z \qquad [12]$$

In these two equations, the expression:

$$B = \sum\sum y_i y_j B_{ij} \qquad [13]$$

Table 2 Visual test of consistency of activity coefficients for binary systems

1. $\log \gamma_1$ evaluated at $x_1 = 0.25$ should be approximately equal to $\log \gamma_2$ evaluated at $x_1 = 0.75$.
2. Let α be the value of $\log \gamma_1$ evaluated at $x_1 = 0$ and β be the value of $\log \gamma_2$ evaluated at $x_1 = 1$.
   $\log \gamma_1$ evaluated at $x_1 = 0.5$ should be approximately equal to 0.25β.
   $\log \gamma_2$ evaluated at $x_1 = 0.5$ should be approximately equal to 0.25α.
3. If α is greater than or equal to β, then the value of $\log \gamma_1$ evaluated at $x_1 = 0.5$ should be less than or equal to the value of $\log \gamma_2$ evaluated at $x_1 = 0.5$.
4. If α is less than β, then the value of $\log \gamma_1$ evaluated at $x_1 = 0.5$ should be greater than the value of $\log \gamma_2$ evaluated at $x_1 = 0.5$.
5. Both $\log \gamma_i$ versus x_i curves show horizontal tangency as x_i approaches unity and $\log \gamma_i$ approaches zero.
6. If there is a maximum (or minimum) on one of the $\log \gamma_i$ versus x_i curves, there is a corresponding minimum (or maximum) on the other curve at the same x_1.
7. If there is neither a maximum nor a minimum on the curves, both curves should be on the same side of the horizontal line that is representing $\log \gamma_i = 0$.

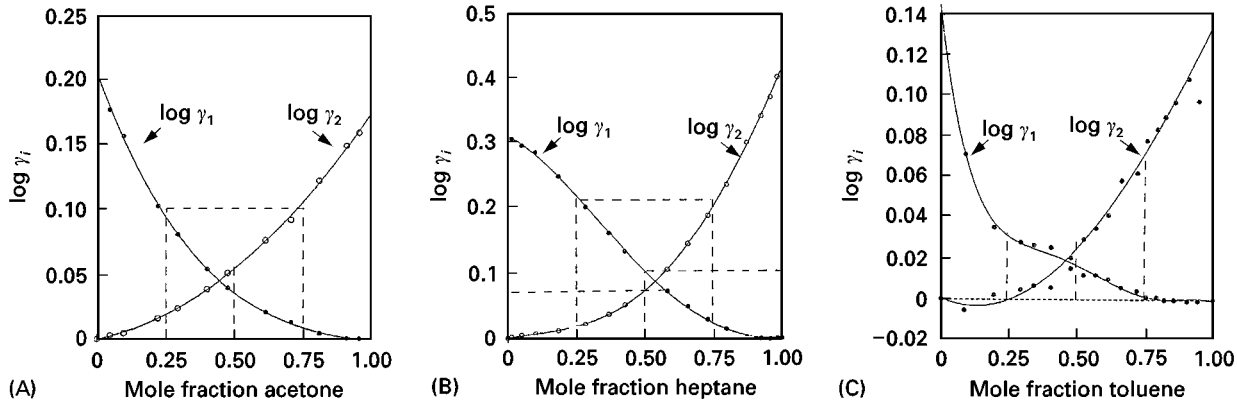

Figure 2 Visual consistency test of binary vapour–liquid equilibrium of (A) the acetone + benzene system at 318.15 K (Brown I and Smith F (1957) Liquid–vapor equilibrium VIII. The system acetone + benzene and acetone + carbon tetrachloride at 45°C. *Australian Journal of Chemistry* 10: 423–428), (B) the heptane + 3-pentanone system at 368.15 K (Geiseler G and Koehler H (1968) Thermodynamic behavior of the binary systems methyl ethyl ketoxime/n-heptane, diethyl ketone/n-heptane, and methyl ethyl ketoxime/diethyl ketone. *Berichte, Bunsengesellschaft fuel Physikalische Chemie.* 72: 697–706), (C) the toluene + n-octane system at 101.3 kPa. (Bromiley EC and Quiggle, D (1933) Vapor–liquid equilibria of hydrocarbon mixtures. *Industrial and Engineering Chemistry* 25: 1136–1138).

is used for the second virial coefficient of the mixture under consideration. When $i \neq j$, the cross second virial coefficient B_{ij} represents the interaction between molecule i and molecule j. Z is the compressibility factor of the mixture. The ϕ_i values obtained from eqns [11] and [12] are practically identical. A generalized method proposed by Hayden and O'Connell in 1975 may be used for predicting the second virial coefficients for pure components and the cross second virial coefficients. For an ideal gas mixture, $\hat{\phi}_i$ is unity.

Expressions are available for representing the dependence of γ_i on the composition of the solution. The activity coefficients are related to the excess Gibbs energy function by the equation

$$G_i^{\mathrm{E}} = RT \ln \gamma_i \qquad [14]$$

where $G_i^{\mathrm{E}} = (\partial n G^{\mathrm{E}}/\partial n_i)_{T,P,nj}$. Some of these expressions, such as the two-parameter equations of van Laar, those of Margules, and the multiparameter equations of Redlich and Kister, are listed in **Table 3**. Additional expressions involving higher-order terms, such as those based on the local composition concept proposed by Wilson in 1964, the nonrandom two-liquid (NRTL) model by Renon and Prausnitz in 1968, and the universal quasi-chemical theory (UNIQUAC) equation by Abrams and Pransnitz in 1975, are frequently applied to activity coefficient calculations for binary and multicomponent systems.

According to eqn [8], the relation between $\ln \gamma_1$ and $\ln \gamma_2$ for a binary system at constant temperature and at low to moderate pressure, is given by:

$$x_i(\mathrm{d} \ln \gamma_1/\mathrm{d}x_1) + x_2(\mathrm{d} \ln \gamma_2/\mathrm{d}x_1) = 0 \qquad [15]$$

which indicates that the two activity coefficients are not independent of each other. These activity coefficients may be evaluated by means of the equations listed in **Table 4**. If the vapour phase can be considered ideal at low pressures, the calculation of γ is much simplified. Pure-component fugacities may be substituted directly by the pure-component vapour pressures:

$$p_i \equiv y_i P = \gamma_i x_i p_i^{\mathrm{sat}} \qquad [16]$$

where p_i is the partial pressure of component i, P the system pressure, and p_i^{sat} the vapour pressure of pure component i.

The effect of temperature on $\ln \gamma_i$ is a concern in data correlation; a suitable representation of the temperature effect permits the determination of data for isobaric conditions from data for isothermal conditions, and vice versa. However, a consistency test for isothermal data is much easier than that for isobaric data because the pressure effect is generally much smaller than the temperature effect. The effect of temperature on $\ln \gamma_i$ is related to the partial molar enthalpy. Lu in 1959 considered the variation of excess enthalpies with temperature for binary systems and suggested that the variation of $\ln \gamma_i$ at constant liquid composition be represented by an expression involving three terms for data interpolation and extrapolation:

$$\ln \gamma_i = a + (b/T) + c \ln T \quad \text{(constant composition)} \qquad [17]$$

In the absence of excess enthalpy data, isothermal data determined at three conditions suffice for the

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Table 3 Selected acitivity coefficient models

Name	$G^E/(RT)$	$\ln \gamma_i$
Margules	$G^E/(RT) = x_1x_2(Ax_1 + Bx_2)$	$\ln \gamma_1 = x_2^2[B + 2(A - B)x_1]$ $\ln \gamma_2 = x_1^2[A + 2(B - A)x_2]$
van Laar	$G^E/(RT) = ABx_1x_2/(Ax_1 + Bx_2)$	$\ln \gamma_1 = A[1 + Ax_1/(Bx_2)]^{-2}$ $\ln \gamma_2 = B[1 + Bx_2/(Ax_1)]^{-2}$
Redlich–Kister	$G^E/(RT) = x_1x_2[A + B(x_1 - x_2) + C(x_1 - x_2)^2 + D(x_1 - x_2)^3 + \cdots]$	$\ln \gamma_1 = a_1x_2^2 + b_1x_2^3 + c_1x_2^3 + d_1x_2^4 + \cdots$ $\ln \gamma_2 = a_2x_1^2 + b_2x_1^3 + c_2x_1^3 + d_2x_1^4 + \cdots$ where: $a_1 = A + 3B + 5C + 7D + \cdots$ $b_1 = -4(B + 4C + 9D) + \cdots$ $c_1 = 12(C + 5D) + \cdots$ $d_1 = -32D + \cdots$ $a_2 = A - 3B + 5C - 7D + \cdots$ $b_2 = 4(B - 4C + 9D) + \cdots$ $c_2 = 12(C - 5D) + \cdots$ $d_2 = 32D + \cdots$
Wilson	$G^E/(RT) = -\sum_i x_i \ln(\sum_j x_j\Lambda_{ij})$	$\ln \gamma_i = 1 - \ln(\sum_j x_j\Lambda_{ij}) - \sum_k [x_k\Lambda_{ki}/(\sum_j x_j\Lambda_{kj})]$
NRTL	$\frac{G^E}{RT} = x_1x_2\left(\frac{\tau_{21}G_{21}}{x_1 + x_2G_{21}} + \frac{\tau_{12}G_{12}}{x_2 + x_1G_{12}}\right)$ where: $\tau_{12} = \frac{\Delta g_{12}}{RT}$, $\tau_{21} = \frac{\Delta g_{21}}{RT}$ $\ln G_{12} = -a_{12}\tau_{12}$, $\ln G_{21} = -a_{12}\tau_{21}$	$\ln \gamma_1 = x_2^2\left[\tau_{21}\left(\frac{G_{21}}{x_1 + x_2G_{21}}\right)^2 + \frac{\tau_{12}G_{12}}{(x_2 + x_1G_{12})^2}\right]$ $\ln \gamma_2 = x_1^2\left[\tau_{12}\left(\frac{G_{12}}{x_2 + x_1G_{12}}\right)^2 + \frac{\tau_{21}G_{21}}{(x_1 + x_2G_{21})^2}\right]$
UNIQUAC	$G^E = G^E(\text{combinatorial}) + G^E(\text{residual})$ $\frac{G^E(\text{combinatorial})}{RT} = x_1 \ln \frac{\Phi_1}{x_1} + x_2 \ln \frac{\Phi_2}{x_2} + 5\left(q_1x_1 \ln \frac{\theta_1}{\Phi_1} + q_2x_2 \ln \frac{\theta_2}{\Phi_2}\right)$ $\frac{G^E(\text{residual})}{RT} = -q_1x_1 \ln(\theta_1 + \theta_2\tau_{21}) - q_2x_2 \ln(\theta_2 + \theta_1\tau_{12})$ $\Phi_1 = \frac{x_1r_1}{x_1r_1 + x_2r_2}$, $\theta_1 = \frac{x_1q_1}{x_1q_1 + x_2q_2}$ $\ln \tau_{21} = -\frac{\Delta u_{21}}{RT}$, $\ln \tau_{12} = -\frac{\Delta u_{12}}{RT}$	$\ln \gamma_i = \ln \frac{\Phi_i}{x_i} + 5q_i \ln \frac{\theta_i}{\Phi_i} + \Phi_j\left(l_i - \frac{r_i}{r_j}l_j\right) - q_i \ln(\theta_i + \theta_j\tau_{ji}) + \theta_jq_i\left(\frac{\tau_{ji}}{\theta_i + \theta_j\tau_{ji}} - \frac{\tau_{ij}}{\theta_j + \theta_i\tau_{ij}}\right)$ where: $i = 1, j = 2$ or $i = 2, j = 1$ $l_i = \frac{z}{2}(r_i - q_i) - (r_i - 1)$ $l_j = \frac{z}{2}(r_j - q_j) - (r_j - 1)$

determination of isobaric data within a reasonable range of temperatures. Similarly, if isobaric vapour–liquid equilibrium data are available at three conditions, isothermal data can be obtained by the same approach and then tested for consistency. The number of sets of vapour–liquid equilibrium data required can be reduced when excess enthalpies are available, but generally one set of experimental values should be used in the correlation. In the absence of the required data for the determination of parameters in eqn [17], $RT \ln \gamma_i$ at a given composition may be assumed to be constant as an approximation. The correlated results can also be used for the prediction purposes.

Equation-of-State Approach

Fugacities of both phases are represented in this approach by the same equation of state, which provides a relationship between the intensive thermodynamic variables T, P, v and composition. Such an equation may be explicit in P or v. The pressure-explicit equations in the form of:

$$P = P(T, v, x_1, x_2, \ldots, x_{n-1}) \qquad [18]$$

are more useful for solving phase-equilibrium problems. In terms of the fugacity coefficients, $\hat{\phi}_{iV}(= \hat{f}_{iV}/y_iP)$ and $\hat{\phi}_{iL}(= \hat{f}_{iL}/x_iP)$, formulation of vapour–liquid equilibria is based on the equilibrium

Table 4 Barker's method for the determination of activity coefficients from experimental data

At equilibrium:

$$\hat{f}_i^{\mathrm{l}} = \hat{f}_i^{\mathrm{v}}$$

$$\hat{\phi}_i^{\mathrm{v}} \equiv \frac{\hat{f}_i^{\mathrm{v}}}{y_i P} \quad \text{(by definition)}$$

$$y_i P \hat{\phi}_i^{\mathrm{v}} = x_i \gamma_i f_i^{\mathrm{l}}$$

$$\hat{\phi}_i^{\mathrm{l}} = \frac{f_i^{\mathrm{l}}}{P}, \qquad \hat{\phi}_i^{\mathrm{sat}} = \frac{f_i^{\mathrm{sat}}}{p_i^{\mathrm{sat}}}$$

Therefore:

$$y_i P \hat{\phi}_i^{\mathrm{v}} = x_i \gamma_i \phi_i^{\mathrm{l}} \mathrm{P}$$

$$\ln (y_i P \hat{\phi}_i^{\mathrm{v}}) = \ln (x_i \gamma_i) + \ln \phi_i^{\mathrm{l}} + \ln P$$

$$= \ln (x_i \gamma_i) + \ln \phi_i^{\mathrm{sat}} + \frac{v_i^{\mathrm{l}}}{RT}(P - p_i^{\mathrm{sat}}) + \ln p_i^{\mathrm{sat}}$$

Hence:

$$\ln \gamma_i = \ln \frac{y_i P}{x_i p_i^{\mathrm{sat}}} + \ln \hat{\phi}_i^{\mathrm{v}} - \ln \phi_i^{\mathrm{sat}} - \frac{v_i^{\mathrm{l}}(P - p_i^{\mathrm{sat}})}{RT}$$

For a binary system:

$$B = y_1^2 B_{11} + 2 y_1 y_2 B_{12} + y_2^2 B_{22}$$

Let:

$$\delta_{12} = 2B_{12} - B_{11} - B_{22}$$

Then:

$$B = y_1 B_{11} + y_2 B_{22} + y_1 y_2 \delta_{12}$$

At low pressure:

$$Z = \frac{P\tilde{v}}{RT} = 1 + \frac{BP}{RT}$$

$$\ln \hat{\phi}_1^{\mathrm{v}} = \left(\frac{B_{11} + y_2^2 \delta_{12}}{RT}\right) P$$

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For pure component i:

$$\ln \phi_i = \int_0^P (Z_i - 1)\frac{\mathrm{d}P}{P}, \qquad \left(Z_i = 1 + \frac{B_{ii}P}{RT}\right)$$

$$\ln \phi_i^{\mathrm{sat}} = \int_0^{p_i^{\mathrm{sat}}} (Z_i - 1)\frac{\mathrm{d}P}{P} = \frac{B_{ii}}{RT} p_i^{\mathrm{sat}}$$

$$\ln \gamma_1 = \ln \frac{y_1 P}{x_1 p_1^{\mathrm{sat}}} + \left(\frac{B_{11} + y_2^2 \delta_{12}}{RT}\right) P - \frac{B_{11}}{RT} p_1^{\mathrm{sat}} - \frac{v_1^{\mathrm{l}}(P - p_1^{\mathrm{sat}})}{RT}$$

$$= \ln \frac{y_1 P}{x_1 p_1^{\mathrm{sat}}} + \frac{(B_{11} - v_1^{\mathrm{l}})(P - p_1^{\mathrm{sat}})}{RT} + \frac{y_2^2 \delta_{12} P}{RT}$$

Similarly:

$$\ln \gamma_2 = \ln \frac{y_2 P}{x_2 p_2^{\mathrm{sat}}} + \frac{(B_{22} - v_2^{\mathrm{l}})(P - p_2^{\mathrm{sat}})}{RT} + \frac{y_1^2 \delta_{12} P}{RT}$$

Barker JA (1953) Determination of activity coefficients from total-pressure measurements. *Australian Journal of Chemistry* (1953) 6: 207–210.

equations:

$$y_i \hat{\phi}_{i\mathrm{V}} = x_i \hat{\phi}_{i\mathrm{L}} \qquad (i = 1, 2, \ldots, N) \qquad [19]$$

with both the $\hat{\phi}_{i\mathrm{V}}$ and $\hat{\phi}_{i\mathrm{L}}$ calculated from the equations:

$$RT \ln \hat{\phi}_i = \int_V^\infty [(\partial P/\partial n_i)_{T,V,nj} - RT/V]\,\mathrm{d}V - RT \ln Z \qquad [20]$$

The advantage of this approach is that it is applicable to calculations of VLE at high pressures and it

can also be used to obtain other configurational properties such as enthalpy, entropy and volume changes of mixing, which are useful in the design of distillation columns.

The first equation of state with a theoretical foundation was proposed by van der Waals in 1873, several decades after the ideal gas equation of state had been formulated. This equation not only yields qualitatively correct representation of the phase behaviour of a real fluid, but also provides the basis of the principle of corresponding states. Hundreds of equations of state have been developed since the publication of the van der Waals equation. They may be theoretical, semi-theoretical or empirical. However, most of the modifications are generally limited to a specific purpose.

In order to apply an equation of state to vapour–liquid equilibrium calculations for pure components, a suitable equation should satisfy the three conditions at a given saturation temperature:

$$v_{V,calc.} = v_V, \qquad v_{L,calc.} = v_L, \qquad f_{V,calc.} = f_{L,calc.} \qquad [21]$$

Mixing and combining rules for the equation parameters are required for extending its application to mixtures. However, most of the practical equations available at present have their inherent advantages and disadvantages and may not satisfy both of the volumetric conditions.

The equations of state expressed in terms of polynomials in volume are of practical importance. For VLE calculations, especially when the properties under consideration are limited to T, P and compositions, the simplest and frequently used form is that which is cubic in v. In spite of their shortcomings, these cubic equations are the most frequently used in practice at present. Currently, the most popular two-parameter cubic equations of state include the Soave–Redlich–Kwong equation (1972):

$$P = RT/(v - b) - a/[v(v + b)] \qquad [22]$$

and the Peng–Robinson equation (1976):

$$P = RT/(v - b) - a/[v(v + b) + b(v - b)] \qquad [23]$$

Both equations can be obtained from a general form of a four-constant cubic equation of the van der Waals type:

$$P = RT/(v - b) - a/[(v + c_1 b)(v + c_2 b)] \qquad [24]$$

Additional multiparameter cubic equations, which are of the form represented by eqn [24] but developed for improving the representations of pure-component vapour pressures, saturated liquid volumes, the critical compressibility factors, and phase behaviour of polar–nonpolar mixtures, appear continuously in the literature. The maximum number of parameters in a cubic equation is five. A list of some selected cubic equations of state is presented in **Table 5**. In some of the cubic equations, different repulsion terms (the first term on the right-hand side of the equations listed in the table) have been adopted. The forms of these equations are frequently influenced by the desire to improve the theoretical basis of the equation, and that of fitting the volumetric properties. It should also be mentioned that one of the inherent limitations of a two-parameter equation is that the critical compressibility factor is a constant for all components. The ability of a cubic equation in VLE representation is controlled by the selection of an adequate temperature function for the parameter 'a' for vapour pressures of pure components, and a set of suitable mixing and combining rules for all the parameters of the equation for mixtures.

Temperature function for 'a' The importance of using a proper temperature function to represent the parameter 'a' cannot be overemphasized. In the 1960s, Wilson began the consideration of the temperature effect on the parameter 'a' of the Redlich–Kwong equation. The expression which has gained wider acceptance was developed by Soave for the same equation in 1972. The parameter 'a' was expressed by:

$$a = a_c \alpha \qquad [25]$$

with α expressed by a function involving the reduced temperature $T_r (= T/T_c)$ in the form:

$$\alpha = [1 + m(1 - T_r^{1/2})]^2 \qquad [26]$$

where the subscript c refers to the critical-point condition, and m represents a quadratic function of the acentric factor of Pitzer. This form and its variations have been adopted subsequently in many cubic equations. A selected set of temperature functions for the parameter 'a' is listed in **Table 6**.

Mixing and combining rules To extend the application of his equation of state to representing the behaviour of mixtures, van der Waals proposed that the constants 'a' and 'b' be expressed by:

$$a = \sum\sum x_i x_j a_{ij} \qquad [27]$$

$$a = \sum\sum x_i x_j b_{ij} \qquad [28]$$

Table 5 Selected cubic equations of state and the corresponding fugacity coefficient expressions

Equation of state	*Fugacity coefficient for pure component i*	*Fugacity coefficient for component i in mixture*[a]
Soave–Redlich–Kwong (1972) $P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)}$	$\ln\phi = Z - 1 - \ln(Z-B) - \frac{A}{B}\ln\left(1+\frac{B}{Z}\right)$ where: $A = \frac{aP}{R^2T^2}$, $B = \frac{bP}{RT}$, $Z = \frac{Pv}{RT}$	$\ln\phi_i = \frac{B_i}{B}(Z-1) - \ln(Z-B) - \frac{A}{B}\left(\frac{2\sum_j y_j a_{ji}}{a} - \frac{B_i}{B}\right)\ln\left[1+\frac{B}{Z}\right]$
Peng–Robinson (1976) $P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)+b(v-b)}$	$\ln\phi = Z - 1 - \ln(Z-B) - \frac{A}{2\sqrt{2}B}\ln\left[\frac{Z+(1+\sqrt{2})B}{Z+(1-\sqrt{2})B}\right]$ where: $A = \frac{aP}{R^2T^2}$, $B = \frac{bP}{RT}$, $Z = \frac{Pv}{RT}$	$\ln\phi_i = \frac{B_i}{B}(Z-1) - ln(Z-B) - \frac{A}{2\sqrt{2}B}\left(\frac{2\sum_j y_j a_{ji}}{a} - \frac{B_i}{B}\right)\ln\left[\frac{Z+(1+\sqrt{2})B}{Z+(1-\sqrt{2})B}\right]$
Patel–Teja (1982) $P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)+c(v-b)}$	$\ln\phi = Z - 1 - \ln(Z-B) + \frac{a}{2RTN}\ln\left[\frac{Z+M}{Z+Q}\right]$ where: $B = \frac{bP}{RT}$, $Z = \frac{Pv}{RT}$ $M = \left(\frac{b+c}{2} - N\right)\frac{P}{RT}$ $N = \left[bc + \frac{(b+c)^2}{2}\right]^{-1/2}$ $Q = \left(\frac{b+c}{2} + N\right)\frac{P}{RT}$	$RT\ln\phi_i = -RT\ln(Z-B) + RT\left(\frac{b_i}{v-b}\right) - \frac{\sum x_j a_{ij}}{d}\ln\left(\frac{Q+d}{Q-d}\right) + \frac{a(b_i+c_i)}{2(Q^2-d^2)} + \frac{a}{8d^3}\{c_i(3b+c) + b_i(3c+b)\} \times\left\{\ln\left(\frac{Q+d}{Q-d}\right) + \frac{2Qd}{Q^2-d^2}\right\}$ where: $Q = v + \frac{b+c}{2}$, $d = \sqrt{bc + \frac{(b+c)^2}{4}}$
Adachi–Lu–Sugie (1983) $P = \frac{RT}{v-b_1} - \frac{a(T)}{(v-b_2)+(v+b_3)}$	$\ln\phi = Z - 1 - \ln(Z-B_1) + \frac{a}{RT(b_2+b_3)}\ln\left(\frac{v-b_2}{v+b_3}\right)$	$\ln\phi_i = \frac{b_{1i}}{v-b_1} - \frac{a}{RT(b_2+b_3)}\left[\frac{b_{2i}}{v-b_2} + \frac{b_{3i}}{v+b_3}\right] + \frac{a}{RT(b_2+b_3)}\left(\frac{2\sum_j y_j a_{ji}}{a} - \frac{b_{2i}+b_{3i}}{b_2+b_3}\right) \times\ln\left[\frac{v-b_2}{v+b_3}\right] - \ln(Z-B_1)$ $\left[b_j = \sum_i x_i b_{ji}\right]$
Iwai–Margerum–Lu (1988) $P = \frac{RT}{v-b} - \frac{a(T)}{v^2+ub(v-b)}$	$\ln\phi = Z - 1 - \ln Z + \ln\left(\frac{v}{v-b}\right) - \frac{1}{RT}\left[\frac{a}{(c^2-4bc)^{0.5}}\right] \times\ln\left[\frac{2v-c+(c^2-4bc)^{0.5}}{2v-c-(c^2-4bc)^{0.5}}\right]$ where: $Z = \frac{Pv}{RT}$, $c = -bu$	$\ln\phi_i = \frac{b_i}{v-b} + \ln\frac{v}{v-b} - \ln Z + \left[\frac{a}{RTA}(v^2-cv+cb)\right] \times[(b_i c + c_i b)(2v-c) + c_i(2bc-cv)] + \left[2\sum_j x_j a_{ij} + \frac{a}{A}\{2(b_i c + c_i b) - cc_i\}\right] \times\frac{1}{RT\sqrt{A}}\ln\frac{2v-c-\sqrt{A}}{2v-c+\sqrt{A}}$ where: $A = c^2 - 4bc$

[a]The mixing rule: $a = \sum_i\sum_j x_i x_j a_{ij}$, $b = \sum_i x_i b_i$, $c = \sum_i x_i c_i$; $a_{ij} = (a_i a_j)^{1/2}(1-k_{ij})$. References: Adachi YB, Lu BC-Y and Sugie H (1983) A four-parameter equation of state. *Fluid Phase Equilibria* 11: 29–48. Iwai Y, Margerum R and Lu BC-Y (1988) A new three-pararmeter cubic equation of state for polar fluids and fluid mixtures. *Fluid Phase Equilibria* 42: 21–41. Patel NC and Teja AS (1982) A new cubic equation of state for fluids and fluid mixtures. *Chemical Engineering Science* 37: 463–473. Peng D-Y and Robinson DB (1976) A new two-constant equation of state. *Industrial and Engineering Chemistry Fundamentals* 15: 59–64. Soave G (1972) Equilibrium constants from a modified Redlich–Kwong equation of state. *Chemical Engineering Science* 27: 1197–1203.

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Table 6 Some different forms of the α function

Form	*Reference*
$\alpha = 1 + m(1 - T_r)$	1
$\alpha = [1 + m(1 - \sqrt{T_r})]^2$	2
$\alpha = [1 + m_1(1 - \sqrt{T_r}) + m_2(1/T_r - 1)]^2$	3
$\alpha = [1 + m_1(1 - \sqrt{T_r}) + m_2(1 - T_r)(0.7 - T_r)]^2$	4
$\alpha = 1 + m_1(1 - T_r) + m_2(1/T_r - 1)$	5
$\alpha = 10^{[m(1 - T_r)]}$	6
$\alpha = \{1 + [m_1 + m_2(1 + \sqrt{T_r})(0.7 - T_r)](1 - \sqrt{T_r})\}^2$	7
$\alpha = 10^{f(T_r)}, \quad f(T_r) = m_3(m_0 + m_1 T_r + m_2 T_r^2)(1 - T_r)$	8
$\alpha = \exp[m_1(1 - T_r) + m_2(1 - \sqrt{T_r})^2]$	9
$\alpha = T_r^{(m_2 - 1)m_3} \exp[m_1(1 - T_r^{m_2 * m_3})]$	10

References: 1. Wilson GM (1964) Vapor–liquid equilibriums, correlation by means of a modified Redlich–Kwong equation of state. *Advances in Cryogenic Engineering*. 9: 168–176. 2. Soave G (1972) Equilibrium constants from a modified Redlich–Kwong equation of state. *Chemical Engineering Science* 27: 1197–1203. 3. Harmens A and Knapp H (1980) Three-parameter cubic equation of state for normal substances. *Industrial and Engineering Chemistry Fundundamentals* 19: 291–294. 4. Mathias PM (1983) A versatile phase equilibrium equation of state. *Industrial and Engineering Chemistry. Process Design and Development* 22: 385–391. 5. Soave G (1984) Improvement of the van der Waals equation of state. *Chemical Engineering Science* 39: 357–369. 6. Adachi Y and Lu BC-Y (1984) Simplest equation of state for vapor–liquid equilibrium calculations: a modification of the van der Waals equation. *American Institute of Chemical Engineers Journal* 30: 991–993. 7. Stryjek R and Vera JH (1986) PRSV: An improved Peng–Robinson equation of state for pure compounds and mixtures. *Canadian Journal of Chemical Engineering* 64: 323–333. 8. Yu JM and Lu BC-Y (1987) A three-parameter cubic equation of state for asymmetric mixture density calculations. *Fluid Phase Equilibria* 34: 1–19. 9. Melhem GA, Saini R and Goodwin BM (1989) A modified Peng–Robinson equation of state. *Fluid Phase Equilibria* 47: 189–237. 10. Twu CH, Bluck D, Cunnigham JR and Coon JE (1991) A cubic equation of state with a new alpha function and a new mixing rule. *Fluid Phase Equilibria* 69: 33–50.

The simplest combining rules for 'a_{ij}' and 'b_{ij}' are obtained by using the geometric mean for a_{ij} and the arithmetic mean for b_{ij}, i.e:

$$a_{ij} = (a_i a_j)^{1/2} \qquad [29]$$

$$b_{ij} = (b_i + b_j)/2 \qquad [30]$$

A binary interaction parameter k_{ij} is frequently introduced in eqn [29] to correct the discrepancy generated by the geometric mean:

$$a_{ij} = (a_i a_j)^{1/2}(1 - k_{ij}) \qquad [31]$$

Occasionally, a binary interaction parameter l_{ij} is introduced in eqn [30] to yield improved b_{ij} values:

$$b_{ij} = (b_i + b_j)(1 - l_{ij})/2 \qquad [32]$$

More recently, new mixing rules, such as the one proposed by Wong and Sandler in 1992, with improved theoretical considerations have appeared in the literature. A list of some mixing and combining rules is presented in **Table 7**.

In general, vapour–liquid equilibrium of a great variety of mixtures, including polar–nonpolar mixtures, can be well represented. For a given mixture, the equation-of-state mixing rules with one set of parameters can frequently represent the data over wide ranges of temperature and pressure.

Examples of binary data representation by means of the two approaches are depicted in **Figure 3**.

Prediction of Vapour–Liquid Equilibria

Although vapour–liquid equilibria have been investigated for more than 10 000 systems, values resulting from various combinations are still unknown. It would be impractical to determine experimentally all the systems needed individually.

In principle, experimental values of some thermodynamic properties can be used to estimate other properties. For examples, binary vapour–liquid equilibrium can be estimated from the liquid activity coefficients calculated from mutual solubility data for the same mixture, and the infinite-dilution activity coefficients measured from gas–liquid chromatography can be used to predict the vapour–liquid equilibria over the complete concentration range. Some prediction methods are briefly described below with emphasis placed on binary mixtures. Extending the

Table 7 Some mixing and combining rules for cubic equations of state

van der Waals/Berthelot

$$a_{ij} = (a_i a_j)^{1/2}$$

$$a = \sum_i \sum_j y_i y_j a_{ij}, \qquad b = \sum_i y_i b_i$$

Modified van der Waals/Berthelot

$$a = \sum\sum y_i y_j a_{ij} \qquad b = \sum\sum y_i y_j b_{ij}$$

$$a_{ij} = (a_i a_j)^{1/2}(1 - k_{ij})$$

$$b_{ij} = \tfrac{1}{2}(b_i + b_j)(1 - c_{ij})$$

Wong–Sandler

$$b - \frac{a}{RT} = \sum_i \sum_j \left(b_{ij} - \frac{a_{ij}}{RT} \right)$$

$$b_{ij} = \frac{b_i + b_j}{2}(1 - k_{ij})$$

$$a_{ij} = \frac{a_i + a_j}{2}(1 - k_{ij})$$

$$\frac{a}{b} = \sum \frac{x_i a_i}{b_i} - \frac{G^E}{CRT}$$

where: G^E is a selected excess Gibbs energy model
C is characteristic of the equation of state

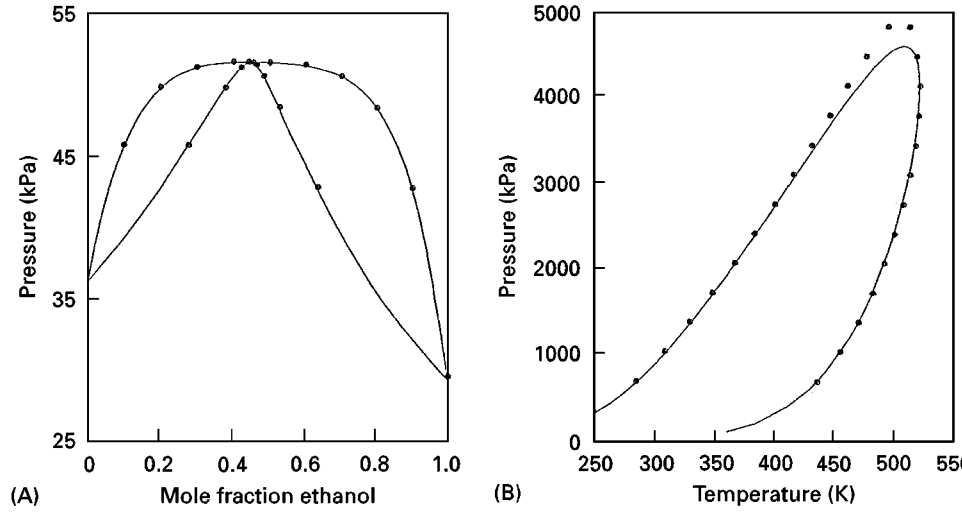

Figure 3 (A) Correlating the phase behaviour of the (ethanol + benzene) system at 323.15 K by means of the gamma–phi approach. The lines represent the values calculated by using the Margules equations and the points represent the experimental values reported by ND. Litvinov (1952) Isothermal equilibrium of vapor and liquid in systems of three fully miscible liquids. *Zhurnal Fizicheskoi Khimii* 26: 1405–1412. (B) Predicting the phase behaviour of the (0.2654 mole fraction ethane + 0.7346 mole fraction *n*-heptane) mixture by means of the equation-of-state approach. The smooth curve represents the values calculated by using the Peng–Robinson equation, and the points represent the experimental values reported by WB Kay (1938) Liquid–vapor phase equilibrium relations in the ethane-n-heptane system. *Industrial and Engineering Chemistry* 30: 459–464.

application to multicomponent mixtures is feasible once good correlation of the vapour–liquid equilibria of its constituent binary systems becomes available.

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Prediction from Pure Component Properties

Application of the regular solution theory For mixtures containing nonpolar components that are not much different in size and shape, the regular solution theory of Hildebrand leads to a semi-quantitative prediction of γ_k values of all components in a mixture. In terms of the solubility parameter, the activity coefficients of the components in a regular solution can be calculated from the equation:

$$RT \ln \gamma_k = v_k(\delta_k - \delta)^2 \qquad [33]$$

where the volume average solubility parameter is given by:

$$\delta = \sum \Phi_i \delta_i \qquad [34]$$

and the volume fraction Φ_i is defined by:

$$\Phi_i = x_i v_i / \sum x_j v_j \qquad [35]$$

The solubility parameter for substance k, δ_k, is defined by:

$$\delta_k = (\Delta U_k^V / v_k^V)^{1/2} = [(\Delta H_k^V - RT)/v_k]^{1/2} \qquad [36]$$

where ΔU_k^V and ΔH_k^V are, respectively, the molar energy and enthalpy of vaporization of pure liquid k at temperature T. The assumption involved here is that T is well below the critical temperature in order to make the approximation valid. The calculated liquid activity coefficients can then be used to obtain the desired vapour–liquid equilibrium values. For a binary mixture:

$$RT \ln \gamma_1 = v_1 \Phi_2^2 (\delta_1 - \delta_2)^2 \qquad [37]$$

$$RT \ln \gamma_2 = v_2 \Phi_1^2 (\delta_1 - \delta_2)^2 \qquad [38]$$

Should a binary interaction parameter be required to improve the data representation, an extension of the approach to the prediction of multicomponent vapour–liquid equilibrium may not be practical; attempts made to correlate the binary parameters have not been successful.

Liquid activity coefficients at infinite dilution γ^∞ Values of γ^∞ are particularly useful for obtaining the parameters of any of the two-constant equations for the excess Gibbs energy; the γ^∞ values for a binary system are the parameter values. For example, $\gamma_1^\infty = A$ and $\gamma_2^\infty = B$ for the van Laar and Margules equations presented in Table 3. If a three-parameter equation is used, the third parameter must be determined by an independent approach.

The modified separation of cohesive energy density (MOSCED) method proposed by Thomas and Eckert

in 1984 may be used to predict γ^{∞} values from pure component parameters. This method is based on a modified regular solution theory and the assumption that the forces contributing to the cohesive energy are additive. It has been reported that the average error of 3357 γ^{∞} values predicted by this method was 9.1%.

In general, calculated equilibrium vapour compositions are relatively insensitive to moderate errors in the γ^{∞} used in the calculation.

Prediction of Binary γ Values Using Azeotropic or Mutual Solubility Data

Prediction from azeotropic data Many binary systems exhibit azeotropic behaviour. At an azeotropic condition, the compositions of the liquid and vapour phases are identical. At low pressures, the liquid activity coefficients can be simply calculated by:

$$\gamma_1 = P/p_1^{\text{sat}} \qquad \text{and} \qquad \gamma_2 = P/p_2^{\text{sat}} \qquad [39]$$

The parameters of any two-parameter expression of the excess Gibbs energy can then be obtained and used for extrapolating vapour–liquid equilibrium over the complete concentration range.

Prediction of γ values from mutual solubility data The thermodynamic consideration applicable to a binary system at vapour–liquid equilibrium is also applicable to a partially miscible binary liquid mixture at equilibrium. Hence, the activity coefficients of the two liquids at the temperature at which the solubilities were experimentally determined can be expressed by:

$$\gamma_1' x_1' = \gamma_1'' x_1'' \qquad \text{and} \qquad \gamma_2' x_2' = \gamma_2'' x_2'' \qquad [40]$$

where the two superscripts refer to the two liquid phases. Applying these relationships to any two-parameter expression of the excess Gibbs energy leads to the determination of the parameter values, which permit vapour–liquid equilibrium estimation of the mixture.

Prediction of γ from Group Contribution Methods

In group contribution methods, the calculation of thermodynamic properties of pure fluids is based on the assumption that each molecule is an aggregate of functional groups. Langmuir in 1925 extended the concept to mixtures. Redlich, Derr, Pierotti and Papadopoulos developed a group interaction model for heats of solution in 1959. Adopting the concepts presented by these authors, Wilson and Deal suggested in 1962 a solution of the groups approach by which liquid activity coefficients can be estimated on the basis of group contributions. In this approach, the logarithm of the activity coefficient of a component is assumed to be the sum of two contributions: the configurational contribution, which accounts for the differences in molecular size, and the group interaction contribution, which accounts for the intermolecular forces originating from the different functional groups.

The group contribution approach to calculating γ is attractive because through this approach it is possible to estimate vapour–liquid equilibria of nonideal mixtures without experimentation. Although a large number of mixtures can result from pure compounds, the functional groups, such as CH_2, OH, CO, COO and COOH, that constitute these compounds are limited. If the activity coefficients of the mixture components could be obtained from a knowledge of the interactions of these groups, and with the assumption that the contribution to γ by one group within a molecule is independent of that made by any other group in that molecule, a relatively small number of parameters would suffice for the prediction of the activity coefficients for mixtures containing the same groups. This assumption implies that the contribution of the group interaction is independent of the nature of the molecule.

Two of these approaches are mentioned here.

Analytical solutions of groups (ASOG) method Following the concept of the solutions of groups of Wilson and Deal, the analytical solutions of groups (ASOG) method was first presented by Derr and Deal in 1969. Basically, the practical application of the solutions of groups concept involves the reduction of liquid activity coefficients obtained from experimental data for vapour–liquid equilibria into a number of binary group interaction parameters. The working equations of the ASOG method are presented in **Table 8**.

Kojima and Tochigi in 1979 calculated the group interaction parameters for 31 groups and used the method to predict the vapour–liquid equilibria for 936 binary systems, 103 ternary systems, five quaternary systems, and two quinary systems at low pressures. They reported that the average absolute deviation of the predicted vapour compositions was 1.2%.

Universal functional group activity coefficient (UNIFAC) method The universal functional group activity coefficient (UNIFAC) method proposed by Fredenslund, Gmehling and Rasmussen and the ASOG method are based on the same principle of group contributions. The main difference between these two methods is in the equations used for

Table 8 The analytical solution of groups (ASOG) method

1. $\ln \gamma_i = \ln \gamma_i^S + \ln \gamma_i^G$
2. $\ln \gamma_i^S = 1 - r_i - \ln r_i$

   where: $r_i = \dfrac{v_i}{\sum x_j v_j}$

   x_j = mole fraction of molecule j

   v_j = number of atoms other than hydrogen in molecule j

3. $\ln \gamma_i^G = \sum_k v_{ki}(\ln \Gamma_k - \ln \Gamma_k^{(i)})$

   where: v_{ki} = number of atoms other than hydrogen in group k in molecule i

   $\ln \Gamma_k = 1 - C_k - \ln D_k$

   $\ln \Gamma_k^{(i)} = 1 - C_k^{(i)} - \ln D_k^{(i)}$

   $$C_k = \sum_j \frac{X_j A_{jk}}{D_j}, \qquad C_k^{(i)} = \sum \frac{X_j^{(i)} A_{jk}}{D_j}$$

   $$D_k = \sum X_j A_{kj}, \qquad D_k^{(i)} = \sum X_j^{(i)} A_{kj}$$

   $$X_L = \frac{1}{S} \sum x_i v_{Li}, \qquad X_L^{(i)} = \frac{v_{Li}}{\sum_k v_{ki}}$$

   $$A_{kL} = \exp\left(m_{kL} + \frac{n_{kL}}{T}\right)$$

   $$S = \sum_i x_i \sum_k v_{ki}$$

representing the excess Gibbs energy. The Wilson equation is used in the ASOG method, whereas the two-parameter universal quasi-chemical (UNIQUAC) equation of Abrams and Prausnitz is used in the UNIFAC method. The working equations of the UNIFAC method are presented in **Table 9**. There are 50 main groups together with their subgroups for the determination of the parameters involved in the calculation. For γ calculations for multicomponent systems, the adjustable binary parameters are evaluated from binary vapour–liquid equilibrium data.

Prediction using Equations of State

The equations of state successfully used for correlation of binary vapour–liquid equilibria can be used for the purposes of predicting multicomponent vapour–liquid equilibria, provided that the binary interaction parameters of all the constituent binary systems are available. All the parameters should be obtained by regression of the binary data using the same mixing and combining rules. Interpolated and estimated values of these parameters are available for some systems, but their values are subject to frequent revision.

Additional Comments on Applications

There is no simple equation of state that can represent satisfactorily the three conditions of eqn [21] over a wide range of temperature. Experience indicates that equations that could meet the equal fugacity condition as well as v_V or v_L would be suitable for the intended vapour–liquid equilibrium calculations. Should a situation arise such that the saturated liquid molar volume is required in the estimation, cubic equations containing more parameters may be selected for the representation. Adachi and Lu in 1990 suggested that it is possible to assign different two-parameter or three-parameter cubic equations to different components of the binary mixture under consideration, and then use a four-parameter cubic equation to combine the equations in the vapour–liquid equilibrium calculations for mixtures.

Special case should be applied when equations of state are used to represent the experimental data measured at or near theoretical points of the fluids.

The selection of mixing and combining rules plays a crucial role in the application of equations of state to the correlation and prediction of vapour–liquid equilibria. The importance of selecting an appropriate expression for the excess Gibbs energy cannot be overemphasized.

The prediction of binary vapour–liquid equilibria from pure-component properties by means of the MOSCED method is attractive. However, poor results are obtained for systems where steric considerations are significant. The general applicability of this model is limited due to the difficulties involved in

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Table 9 The UNIFAC method

1. $\ln \gamma_i = \ln \gamma_i^c + \ln \gamma_i^R$
2. $\ln \gamma_i^c = 1 - J_i + \ln J_i - 5q_i\left(1 - \dfrac{J_i}{L_i} + \ln \dfrac{J_i}{L_i}\right)$

   where: $J_i = \dfrac{r_i}{\sum_j x_j r_j}, \qquad L_i = \dfrac{q_i}{\sum x_j q_j}$

   $r_i = \sum_k v_k^{(i)} R_k, \qquad q_i = \sum_k v_k^{(i)} Q_k$

   R_k = volume parameter for group k

   Q_k = surface area parameter for group k

   $v_k^{(i)}$ = number of subgroups of type k in molecule of species i
3. $\ln \gamma_i^R = q_i\left[1 - \sum_k \left(\dfrac{\theta_k \beta_{ik}}{S_k} - \rho_{ki} \ln \dfrac{\beta_{ik}}{S_k}\right)\right]$

   where: $\rho_{ki} = \dfrac{v_k^{(i)} Q_k}{q_i}$

   $\beta_{ik} = \sum_m \rho_{mi} \tau_{mk}$

   $\theta_k = \dfrac{\sum_i x_i q_i \rho_{ki}}{\sum_j x_j q_j}$

   $S_k = \sum_m \theta_m \tau_{mk}$

   $\tau_{mk} = \exp\left(-\dfrac{\alpha_{mk}}{T}\right)$

   α_{mk} = group interaction parameter

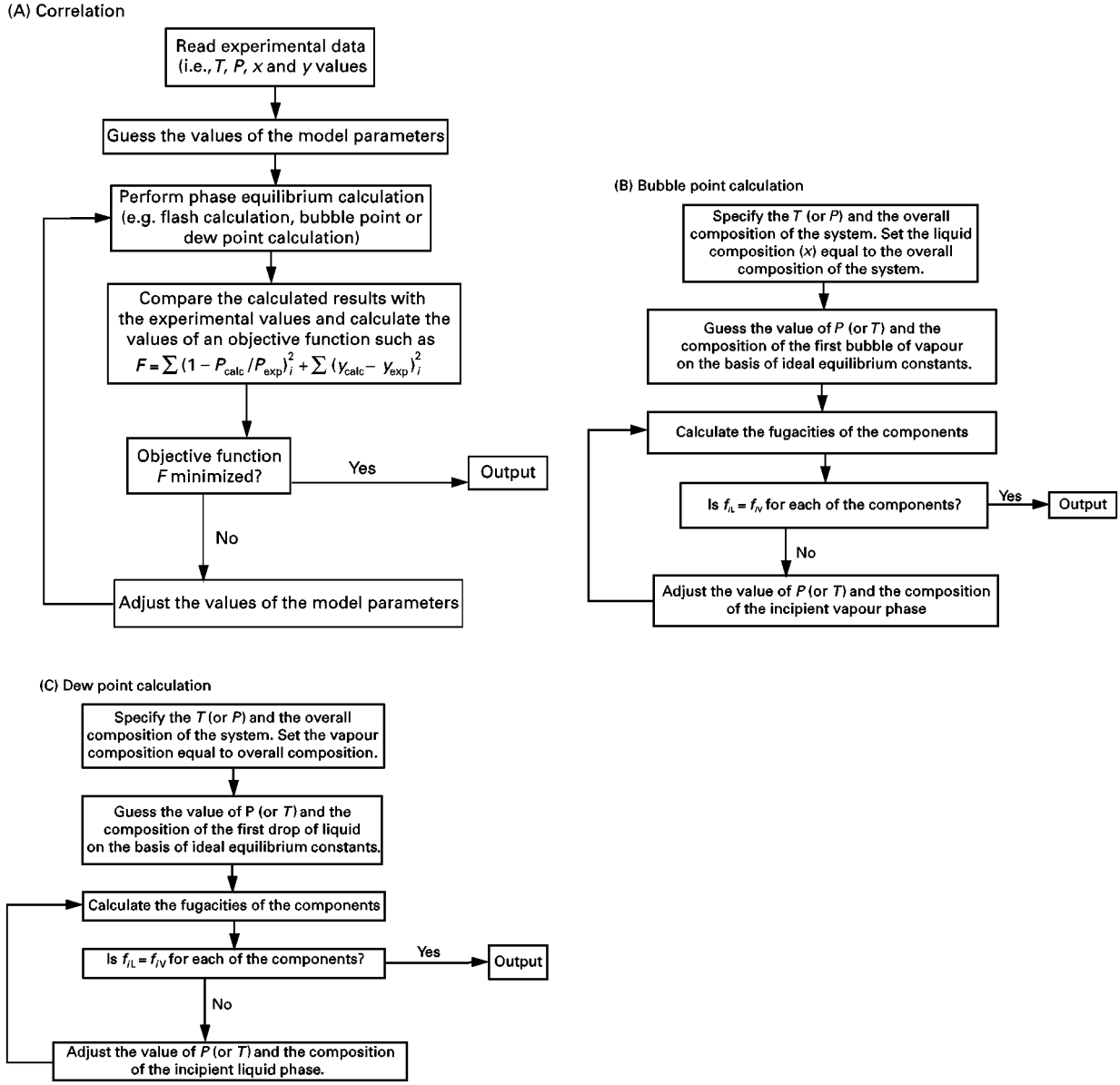
(A) Correlation
Read experimental data (i.e., T, P, x and y values
Guess the values of the model parameters
Perform phase equilibrium calculation (e.g. flash calculation, bubble point or dew point calculation)
Compare the calculated results with the experimental values and calculate the values of an objective function such as
$F = \sum (1 - P_{calc}/P_{exp})_i^2 + \sum (y_{calc} - y_{exp})_i^2$
Objective function F minimized?
Yes
Output
No
Adjust the values of the model parameters
(B) Bubble point calculation
Specify the T (or P) and the overall composition of the system. Set the liquid composition (x) equal to the overall composition of the system.
Guess the value of P (or T) and the composition of the first bubble of vapour on the basis of ideal equilibrium constants.
Calculate the fugacities of the components
Is $f_{iL} = f_{iV}$ for each of the components?
Yes
Output
No
Adjust the value of P (or T) and the composition of the incipient vapour phase
(C) Dew point calculation
Specify the T (or P) and the overall composition of the system. Set the vapour composition equal to overall composition.
Guess the value of P (or T) and the composition of the first drop of liquid on the basis of ideal equilibrium constants.
Calculate the fugacities of the components
Is $f_{iL} = f_{iV}$ for each of the components?
Yes
Output
No
Adjust the value of P (or T) and the composition of the incipient liquid phase.

Figure 4 Algorithms for correlating and predicting vapour–liquid equilibrium values.

the determination of pure component parameters. Furthermore, the approach cannot be used for aqueous mixtures, nor for systems with very large γ^{∞} values.

In general, the accuracy of prediction depends on the availability of some reliable binary data for either the system of interest or another one that is closely related to it.

All the group-contribution methods are approximate. The fundamental assumption involved in the group solution approach is additivity, and the estimated γ values are necessarily approximate.

Finally, computer software packages for vapour–liquid equilibrium calculations are available commercially from a number of process engineering software development companies. Typical algorithms for data correlation and prediction are depicted in **Figure 4**.

See also: **II/Distillation:** Modelling and Simulation; Multicomponent Distillation; Theory of Distillation; Vapour-Liquid Equilibrium: Theory. **III/Physico-Chemical Measurements: Gas Chromatography.**

Further Reading

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DropBooks

Vapour–Liquid Equilibrium: Theory

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Introduction

The concept of an equilibrium stage in distillation is based on the assumption that the vapour leaving the stage is in equilibrium with the liquid leaving the same stage. The use of this concept in the design of distillation columns requires a description of how the components of a multicomponent mixture distribute between the two phases in equilibrium. This description is provided by phase equilibrium thermodynamics.

The equilibrium relationship for any component i in an equilibrium stage is defined in terms of the